



Short communication

Electrochemical characteristics of rechargeable polyaniline/lead dioxide cell

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HIGHLIGHTS

- ▶ PANI and PbO₂ electrode was synthesized from sulfuric acid solution.
- ▶ Electrode was investigated for PANI/PbO₂ rechargeable cell.
- ▶ Electrochemical characteristic of the cell was determined.

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ABSTRACT

Electrochemically synthesized polyaniline (PANI) and lead dioxide have been investigated as electrode materials for PANI/1.1 M H₂SO₄; 0.5 M (NH₄)₂SO₄/PbO₂ rechargeable cell. At constant current charge/discharge of the cell, the average discharge potential of 1.1 V, specific capacity of 50 mA h g⁻¹, specific energy of 55 W h kg⁻¹, and self discharge rate of 2.2% per day have been obtained.

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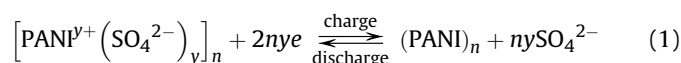
1. Introduction

Replacement the Pb negative electrode with polyaniline (PANI) could avoid some of the problems with negative Pb electrode compared to classical Pb/PbO₂ systems [1–3]. Additionally, both the specific energy and the specific power could increase significantly, owing to the much smaller mass of PANI electrode compared to classical Pb negative electrode. Moreover, lower concentration of sulfuric acid and decrease of lead content in such cell increase its ecological acceptability of such cell.

In our previous work, electrochemical characteristics of polyaniline (PANI) and lead dioxide (PbO₂) electrodes were investigated in 1.1 M H₂SO₄, aiming to characterize thin film PANI and PbO₂ electrode for the potential application in aqueous based PANI/H₂SO₄/PbO₂ cell. [1]. Considering electrochemical behavior, for

different doping (oxidation) potential limits, and dedoping capacity of PANI electrode in 1.1 M H₂SO₄ it was suggested that doping potential should not exceed 0.4 V. The obtained specific electrode capacity of PANI electrode was 240 mAh g⁻¹. This value was obtained considering only the electroactive mass (0.48 g) of the total deposited PANI mass (2.1 mg). So, the realistic value of the specific electrode capacity will be around 50 mA h g⁻¹. By simulation of the charge/discharge characteristic, based on the half cell reactions, it was estimated that cell charging voltage would range between 1 and 1.9 V, while discharge would occur between 1.35 and ~0.8 V, with most of the charge delivered at above 1 V.

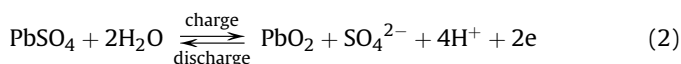
In the PANI/PbO₂ system, the half cell reaction for charge and discharge can be given as [1]:



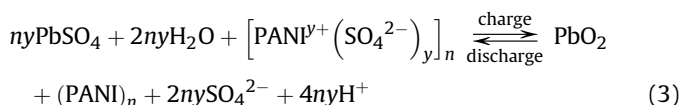
where y is doping degree, and:

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The overall reaction in the cell would be:



It is very important to bear in mind that, according to given schema, during cell charging, PANI would be dedoped, on contrary, during cell discharge, PANI would be doped.

It is interesting to note that from early work on PANI, Pb and PbO₂ cells, by Kitani et al. [4], until now, practically no data on electroconducting polymers (ECP)/PbO₂ cells were provided in the literature. There were attempts to improve characteristics of negative, Pb electrode, and prevent grids corrosion by PANI coatings, conducted by Martha et al. and Cheraghi et al. [5–7].

After the reexamining of the results in 1.1 M H₂SO₄, it was concluded that PbO₂ electrode had poor cyclization characteristics and low coulombic efficiency in this electrolyte. In the present study we have used the novel electrolyte consisted of 1.1 M sulfuric acid and 0.5 M ammonium sulfate which has good buffer capacity and benefits to PbO₂ electrode [8].

Hence, the aim of this work was investigation of electrochemically synthesized polyaniline and lead dioxide as the electrode materials for PANI/1.1 M H₂SO₄; 0.5 M (NH₄)₂SO₄/PbO₂ cell.

2. Experimental

Thin film PANI electrode was electrochemically synthesized from aqueous 1.1 M sulfuric acid solution with addition of 0.25 M aniline monomer (p.a. Merck, previously distilled in argon atmosphere). The polymerization was performed on graphite electrode (*S* = 18 cm²), galvanostatically at constant current of 36 mA, during 5000 s, with the total polymerization charge of 50 mA h. After polymerization, PANI electrode was discharged with the current of 18 mA to test the film quality, washed with bidistilled water and transferred into another electrochemical cell for further investigations.

The mass of PANI was determined by measuring the graphite electrode before and after electropolymerization, followed by overnight drying in vacuum.

Lead dioxide electrode was prepared on pure lead (99.95%) (*S* = 18 cm²), according to Planté formation process described in detail by Petersson et al. [9,10]. In order to remove lead oxides, naturally formed in the air, the lead sample was dipped in 8 M HNO₃ for 30 s, and rinsed in bidistilled water prior to immersion in 0.5 M H₂SO₄ and 0.05 M KClO₄ (p.a. Merck) for the formation process. The lead electrode was initially pretreated cathodically at constant current of 36 mA during 25 min, and then oxidized and reduced galvanostatically in the same electrolyte at current of 36 mA. After formation process, the remains of perchlorate ions were removed from the electrode by rinsing in bidistilled water. Finally, the PbO₂ electrode was completely oxidized in pure 1.1 M H₂SO₄ with the current of 36 mA during 1500 s.

For all further electrochemical experiments electrolyte consisted of 1.1 M sulfuric acid and 0.5 M ammonium sulfate was used.

Prior to investigation, working electrode was mechanically polished firstly with fine emery papers (2/0, 3/0 and 4/0, respectively) and then with polishing alumina of 1 μm (Banner Scientific Ltd.) on the polishing cloths (Buehler Ltd.). After mechanical polishing the traces of the polishing alumina were removed from the electrode surface ultrasonically in ethanol during 5 min.

Electrochemical synthesis and characterization of PANI and PbO₂ electrodes were performed in a single compartment

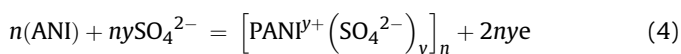
electrochemical cell with total volume of 100 cm³. Platinum mesh (*S* = 18 cm²) was used as counter, while saturated calomel electrode, SCE, (*E_r* = 0.243 V vs. SHE), served as reference electrode. For the characterization of the PANI/PbO₂ cell the same electrochemical cell, with electrode gap of 1 cm, was used.

The electrochemical measurements were carried out using PAR M273 potentiostat/galvanostat controlled by a computer, while voltage data was collected using ISO-Tech IDM 73 multimeter connected to the computer via RS 232.

3. Results and discussion

3.1. Synthesis and characterization of PANI electrode

Fig. 1 shows the chronopotentiometric curve of aniline polymerization on graphite electrode at constant current of 36 mA, during 5000 s with the polymerization charge, *q_{pol}*, of 50 mA h from aqueous solution of 1.1 M H₂SO₄ and 0.25 M aniline (ANI) monomer. Aniline polymerization, in sulfuric acid solution, proceeded in the potential range between 0.7 and ~0.52 V according to the equation:



The mass of PANI deposited on graphite electrode, determined in a separate experiment after drying in vacuum overnight, was 0.0989 g. The corresponding thickness of PANI electrode, assuming the density of sulfate doped PANI of 1.43 g cm⁻³, was estimated to ~40 μm [11].

Insert of Fig. 1 shows cyclic voltammogram of the PANI electrode in 1.1 M sulfuric acid and 0.5 M ammonium sulfate, for the anodic potential limit of 0.5 V. Doping of the PANI electrode with sulfate anions started at ~-0.1 V and proceeded up to the potential of 0.4 V. The well defined peak at 0.2 V, could be attributed to the changes of the doping degree of PANI between *y* > 0 and 0.5. It should be noted that at low negative potentials leucoemeraldine form (*y* ≈ 0) could exist as well [12]. Above potentials of ~0.4 V the possibilities of formation the quinone-like degradation products is expected [1,13].

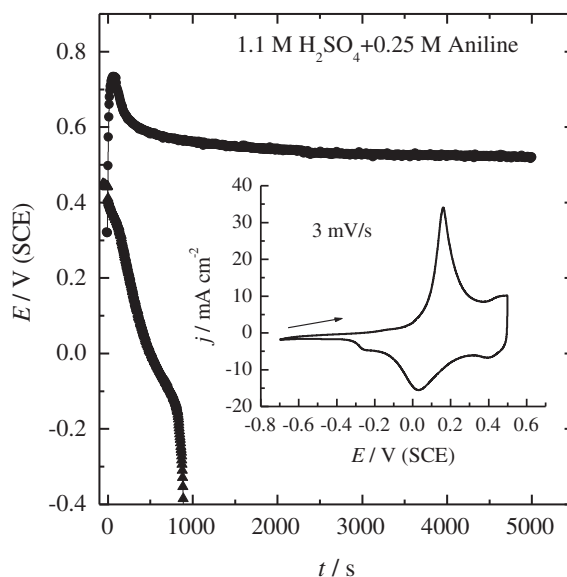


Fig. 1. Galvanostatic curves of aniline electropolymerization (*I* = 36 mA) and discharge (*I* = 18 mA). Insert: cyclic voltammogram of PANI electrode in 1.1 M sulfuric acid and 0.5 M ammonium sulfate.

In the cathodic scan, reduction of degradation products and emeraldine salt to leucoemeraldine proceeded in the potential range between 0.5 and -0.3 V.

Doping/dedoping curves of PANI electrode for different currents, and for doping potential limit of 0.4 V are shown in Fig. 2. Curves are characterized by constant increase/decrease of the potential which is connected to the changes of the emeraldine salt doping degree given by overall reaction:



Fig. 3 shows calculated values of doping/dedoping electrode capacity and specific capacity for different currents. As it can be seen electrode capacity was dependent on the applied current, and decreased from 7 (6.5) to 5.5 mA h, or from 70 (65) to 55 mA h g $^{-1}$ with increasing the current. Decrease in the electrode capacity with increasing of the current, is connected with slow diffusion of sulfate anions through polymer film. Coulombic efficiency, shown in the insert of Fig. 3, for the current higher than 30 mA was $\sim 100\%$, while for the current lower than 30 mA, was higher than 100% (103 – 108%). This unusual results, as pointed out in our previous paper, could be explained by the possibilities of hydrogen evolution reaction ($E_r = -0.24$ V) or even more probably by formation of protonated leucoemeraldine at low current and negative potentials [1]. Such additional charge was, after current interruption, quickly discharged, at the PANI electrode open circuit potentials of -0.05 V and was not observed during charge.

As pointed out, the degradation of PANI could occur above ~ 0.4 V. So, behavior of PANI electrode during cyclization, at a constant current of 36 mA for charging potential limits of 0.35 and 0.45 V, was investigated, and shown in Fig. 4. As it can be seen in Fig. 4, during first ten cycles for charging with potential limit of 0.35 V, discharge time remained constant. Charging of the electrode to the potential of 0.45 V, during nine cycles, provoked some small decrease of the discharge times, inducing the additional decrease of the discharge time for potential limits of 0.35 V during twentieth cycle. Hence, it could be suggested that charging potential limits should not exceed 0.4 V.

3.2. Synthesis and characterization of PbO₂ electrode

Fig. 5 shows galvanostatic synthesis of PbO₂ on the oxide free lead electrode at constant current of 36 mA in aqueous solution of 0.5 M H₂SO₄ and 0.05 M KClO₄, according to the similar procedure

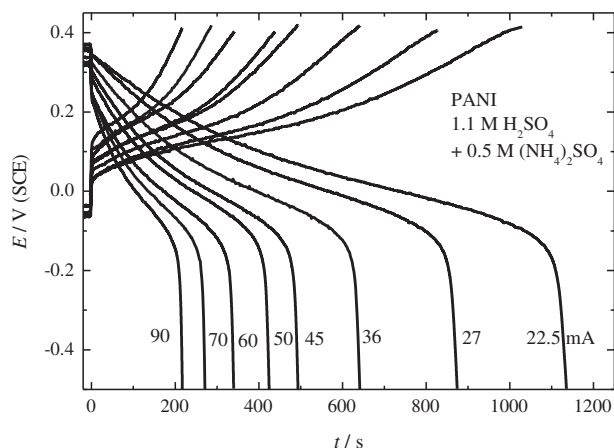


Fig. 2. Doping/dedoping curves of PANI electrode for different currents, marked in figure.

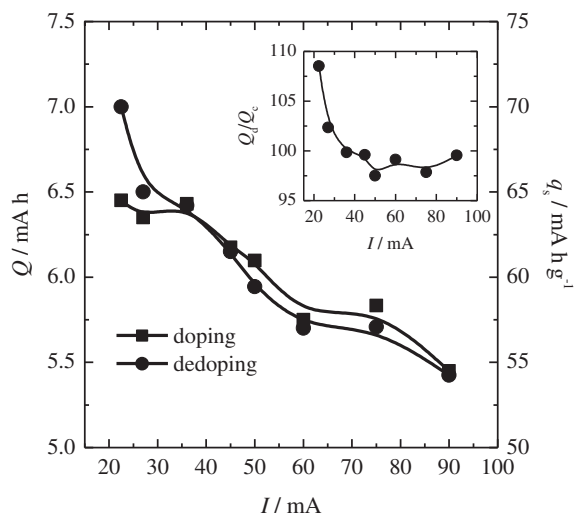


Fig. 3. Calculated values of PANI electrode capacity (Q) and specific capacity (q_s) for different currents. Insert: Coulombic efficiency.

described by Petersson et al. [9,10]. Initially, the electrode was treated cathodically for 1500 s at 36 mA and then oxidized and reduced galvanostatically in the same electrolyte. After current was applied, during 10 s, potential had the similar value as the open circuit potential, ~ -0.52 V. This time could be assigned to the induction period, t_{ind} , of the PbSO₄ formation. When most of the lead surface was converted into PbSO₄, increase of the potential up to the ~ 1.7 V followed by a plateau at ~ 1.55 V, could be connected to transformation of PbSO₄ into PbO₂. After 700 s, electrode was discharged to ~ 0.7 V, with the same current. According to Fig. 5 the total time, which could be connected to the formation of PbO₂, was 700 s (or 7 mA h). Relying to Faradays law, and assuming formation process efficiency of 100% [9,10], the calculated mass and corresponding thickness of the PbO₂ electrode, were 31 mg and 1.85 μm respectively.

Charge/discharge curves of PbO₂ electrode, for different currents, in 1.1 M sulfuric acid and 0.5 M ammonium sulfate are shown in Fig. 6. Charge of the electrode started at 1.4 or 1.5 V, depending on applied current, followed by slow increase of the potential. After that period of time, faster increase of the potential could be connected to oxidation of small amounts of PbSO₄

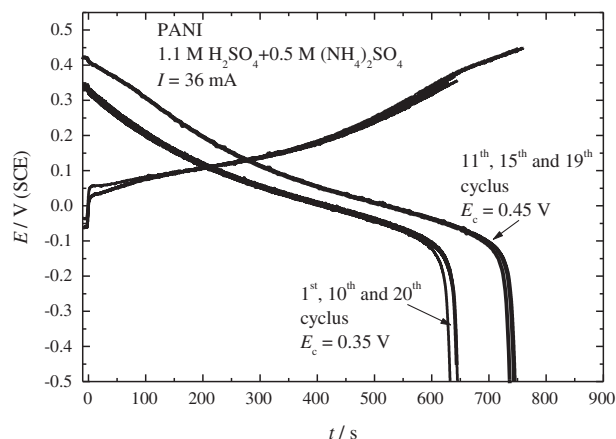


Fig. 4. Potential-current curves of PANI electrode during cyclization at a constant current of 36 mA for charging potential limits of 0.35 and 0.45 V.

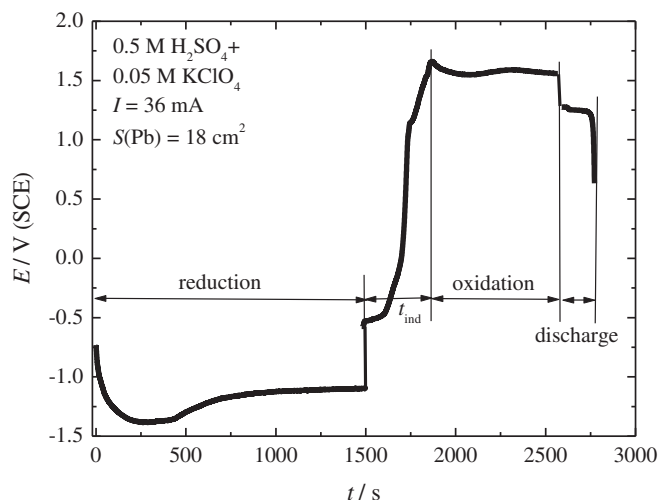


Fig. 5. Dependence of potential on time during galvanostatic formation of PbO_2 electrode.

remains, and oxygen evolution. Discharge of the PbO_2 occurred via one well defined potential plateau of 1.27 ± 0.01 V.

From Fig. 6 the capacities of charge/discharge processes were calculated and shown in Fig. 7. Charge capacity increased non-linearly from 8.5 to 9.7 mA h with increasing current. On contrary, discharge capacity of ~ 7 mA h was practically independent on applied current. Coulombic efficiency of charge/discharge, shown in the insert of Fig. 6, for the current lower than 30 mA, ranged from 81 to 82.5%, while for the current higher than 30, decreased from 82 to 73%.

During the cyclization of PbO_2 electrode (Fig. 8), small decrease of charging and increase of discharging potentials, and practically constant capacity were observed. Decrease of the peak during cyclization, was also observed for the first 100 s of the charging process, and could be connected to oxidation of PbSO_4 phase.

3.3. Electrochemical characteristic of PANI/ PbO_2 cell

Comparing the results for PANI and PbO_2 electrode it can be concluded that disbalance in the charge/discharge time, for the same current existed. In Fig. 9 charge/discharge curves for PbO_2

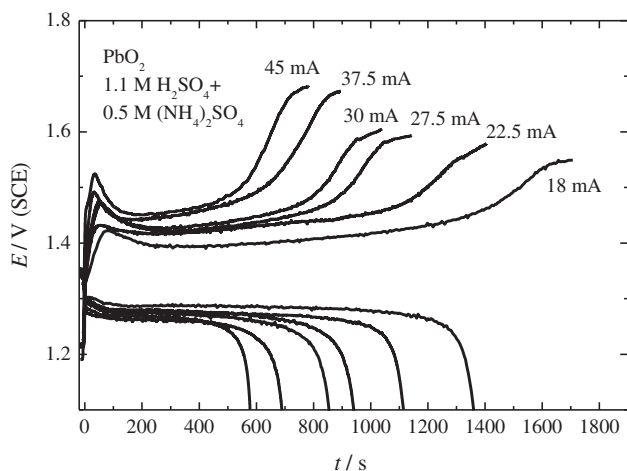


Fig. 6. Charge/discharge curve of PbO_2 electrode for different currents, marked in figure.

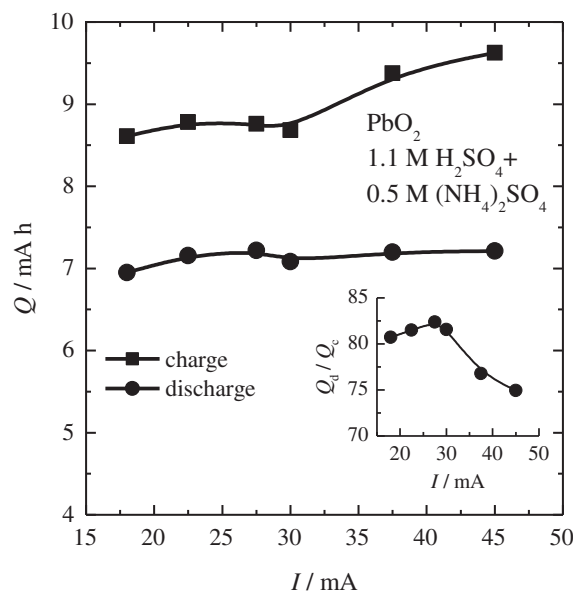


Fig. 7. Dependence of charge/discharge capacity of PbO_2 electrode for different current. Insert: Coulombic efficiency of charge/discharge.

electrode at current 22.5 mA ($j = 1.25$ mA cm^{-2}) and 27.5 mA ($j = 1.53$ mA cm^{-2}), and for PANI electrode of 22.5 mA ($j = 1.25$ mA cm^{-2}) are shown. As it can be seen, charge/discharge times, were practically equal for the PbO_2 current of 27.5 mA and 22.5 mA for the PANI electrode. To avoid this problem we reduced the surface area of PbO_2 electrode to 14.7 cm^2 . Now, for the overall cell current of 22.5 mA, current density for PbO_2 electrode was 1.53 mA cm^{-2} , and for PANI electrode 1.25 mA cm^{-2} .

With such surface reduced PbO_2 electrode, the charge/discharge characteristics of the complete cell, during ten cycles with current of 22.5 mA, were investigated and shown in Fig. 10. Charging of the cell started at ~ 0.85 V, followed by voltage increase up to 1.5 V. The shoulder in the potential range of 1.5–1.8 V could be associated to behavior of PbO_2 electrode, and sharp increase of the voltage above

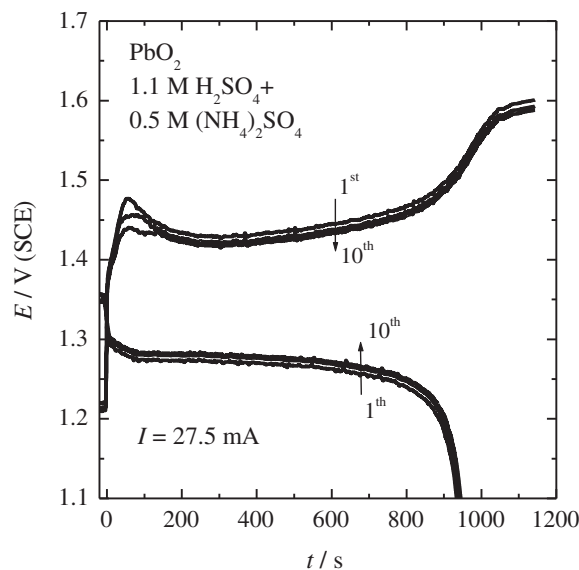


Fig. 8. Potential-current curves of PbO_2 electrode during cyclization at a constant current of 27.5 mA.

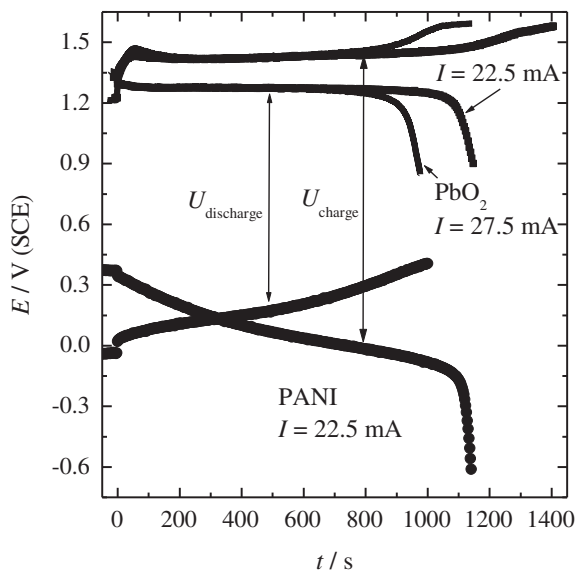


Fig. 9. Comparison of charge/discharge curves for PbO₂ and PANI electrode.

1.8 V to PANI electrode. Open circuit voltage of charged cell was 1.4 V. Discharge of the cell occurred in the potential range of 1.4 to 0.8 V, followed by the sharp decrease of the voltage, which can be connected to behavior of PbO₂ electrode. Average discharge voltage was ~1.1 V, comparable to those of cadmium/nickel oxide and metal hydride/nickel oxide batteries. It should be noted that discharge of the cell below 0.4 V could affect PANI electrode, due to the possibilities of degradation. Decrease of the charge/discharge times during cyclization was most probably connected to some electrode capacity disbalance, rather than active mass degradation.

Self discharge rate was investigated after five days, and results are shown in Fig. 11. After five days, decrease of the open circuit potential from 1.4 V to 1.32 V, and discharge time of 11% were observed, giving self discharge rate of 2.2% per day. The reasons of such high self discharge rate were probably connected to both electrodes. Thin film PbO₂ was probably discharged due to the presence of the organic impurities from PANI electrode. Self discharge of PANI electrode, as proposed by Rahmanifar et al. [14],

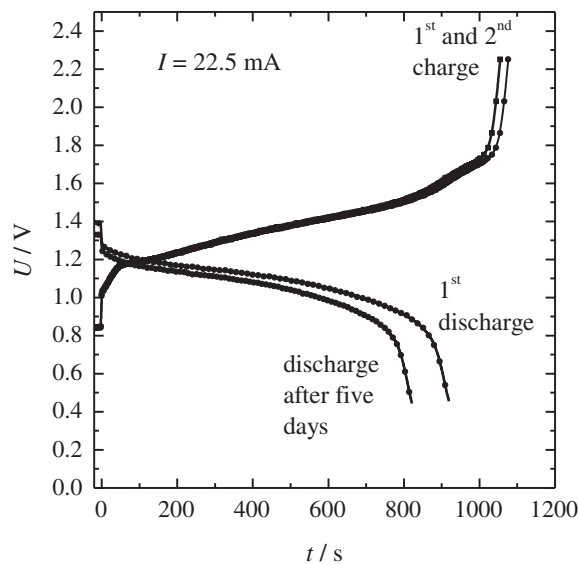
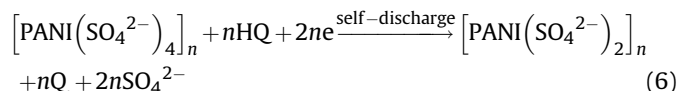


Fig. 11. Determination of the self discharge rate of PANI/PbO₂ cell.

occurred as a consequence of the reaction of soluble hydroquinone (HQ) like species with pernigraniline salt form of PANI, giving protonated emeraldine, via simplified reaction:



Based on the above given redox reaction, HQ is formed under the conditions at which PANI existed in the pernigraniline form, and then the resulting HQ reacted with the remaining pernigraniline and converted it to the emeraldine conductive form. This could be the main cause of the reduced open circuit potential and the capacity.

Knowing the masses of PANI (0.0989 g) and PbO₂ (25.4 mg, initial mass of PbO₂ reduced for 18%) it was possible to draw the diagram of charge/discharge over specific capacity of the cell. As it

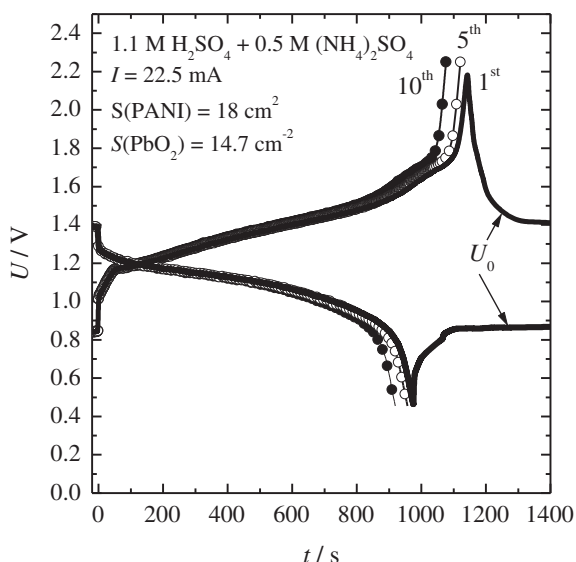


Fig. 10. Charge/discharge curves of PANI/PbO₂ cell during cyclization.

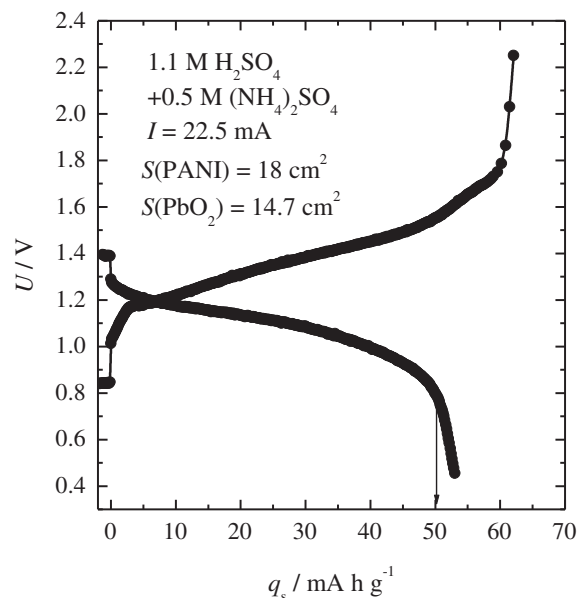


Fig. 12. Dependence of charge/discharge voltage on specific capacity of the PANI/PbO₂ cell.

can be seen in Fig. 12 available specific discharge capacity was 50 mA h g^{-1} of active electrode mass, with active mass utilization of 83%. For the average discharge voltage of 1.1 V, specific discharge energy of 55 W h kg^{-1} was calculated.

4. Conclusions

Polyaniline and lead dioxide electrode were successfully synthesized from sulfuric acid based solutions. Charge/discharge characteristic of the separate electrodes was investigated in 1.1 M sulfuric acid and 0.5 M ammonium sulfate electrolyte. Based on this results, electrodes were balanced and characteristics of polyaniline/lead dioxide cell were investigated. At the charge/discharge current of 22.5 mA the average discharge potential of 1.1 V, specific capacity of 50 mA h g^{-1} , specific energy of 55 W h kg^{-1} , and self discharge rate of 2.2% per day were obtained. High self discharge rate was connected to reaction of soluble hydroquinone like species formed during the polyaniline charging.

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